

# THIN FILM ELECTRODES WITH AN INTEGRAL CURRENT COLLECTION GRID FOR USE WITH SOLID ELECTROLYTES

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## ABSTRACT

Thin film, high performance electrodes which can operate in high temperature environments are necessary for many devices which use a solid electrolyte. Electrodes of rhodium-tungsten alloy have been deposited on solid electrolyte using photolytic chemical vapor deposition (PCVD). A technique for depositing electrodes and current collection grids simultaneously has been developed using the pre-nucleation characteristic of PCVD. This technique makes it possible to fabricate electrodes which allow vapor transport through the thin ( $<1 \mu\text{m}$ ) portions of the electrode while integral thick grid lines improve the electronic conductivity of the electrode, thus improving overall performance.

## INTRODUCTION

Electrochemical devices which use a solid electrolyte generally require thin film electrodes to allow vapor passage through the electrode. Such devices include, but are not limited to energy conversion devices such as fuel cells and the alkali metal thermal to electric converter (AMTEC), and electrochemical pumps and electrolysis cells. Requirements of thin film electrodes used with solid electrolytes include (a) sufficient porosity or a transport mechanism to allow passage of fuel or working fluid as vapor from the electrode/electrolyte interface through the electrode, (b) electronic conductivity, and (c) refractory characteristics for operation at high temperature, possibly in corrosive environments. The challenge in designing electrodes which combine all three characteristics is in making electrodes which are sufficiently thin and sufficiently conductive at the same time.

Work has been ongoing in recent years to find the optimum conditions to meet the above requirements; the approach to obtaining both conductivity and transport which has been used at the Jet Propulsion Laboratory has been to combine a thick film grid with a thin film electrode. The grid acts as a current collection network in the electrode, by increasing electronic conduction and the capability for vapor transport is maintained in the thin film areas (1). Grids have been deposited on solid

electrolyte using photolytic chemical vapor deposition (PCVD) of metals from organometallic precursors such as metal carbonyls. When an electrode with current collection grids was tested in an AMTEC device, overall performance increased 25-50% (measured power production), presumably because of decreased resistance in the electrode, in spite of 10-15% of the surface area of the electrode being occluded to vapor flow by thick grid lines (1).

In earlier work at JPL, we have deposited grid lines using PCVD of a refractory metal such as molybdenum, followed by sputter deposition of a metal alloy electrode such as platinum-tungsten or rhodium-tungsten (1,2). While device performance was significantly improved, there are drawbacks to this approach to making grids. An oxide layer may form on the surface of the grid before the electrode is sputter deposited over it, resulting in a contact resistance between the grid and the electrode. In addition, the differences in the coefficients of thermal expansion between the grid material and the electrode material may result in buckling or peeling of the electrode at the grid lines during operation at high temperature. Finally, the rate of grain growth of Mo metal is relatively rapid at temperatures above 1100 K and the operating lifetime of a device may be significantly shortened if Mo grids are used, even in combination with longer lived electrode materials (2). Interdiffusion of Mo films with Pt<sub>3</sub>W or Rh<sub>3</sub>W films may result in formation of ternary alloys with higher resistance and/or more rapid grain growth.

The drawbacks associated with photodeposited molybdenum grids and sputter deposited alloy electrodes may be avoided by constructing integral grids and electrodes, where the grid and electrode have the same composition and are deposited on the electrolyte simultaneously. In this way, there are no contact resistances between the grid and the electrode, and there is no difference in coefficient of thermal expansion between the electrode and the grid. As alloys of noble metals (platinum or rhodium) with tungsten have been determined to be among the best performing AMTEC electrodes (3), it has been necessary to develop techniques for PCVD of metal alloys and to investigate the mechanism of deposition of two metals in the presence of each other (4).

### Photolytic Chemical Vapor Deposition

Photolytic CVD is a well established technique which has been applied to deposition of metals on metal, semiconductors, and insulating substrates (5-9). It is accomplished by irradiating a substrate which is surrounded by low pressure metal-organic vapor with UV light; in the studies presented here, metal carbonyls were used as metal-organic precursors to the metal. Light is imaged on the substrate in the pattern desired, or alternatively the substrate is physically masked and then irradiated. Metal carbonyl dissociates as a result of absorption of UV light; the released metal condenses on the substrate surface in the illuminated area. PCVD has several advantages for thin film electrode deposition. Metals are deposited only in illuminated areas, so that deposits may be patterned or arranged in domains. It is possible to write micrometer sized patterns on a substrate using photodeposition

(5,6,10). The mode of attachment or extent of bonding to the ceramic electrolyte appears to be different for photodeposited and sputter deposited films as we have found that photodeposited films are significantly more adherent than sputter deposited films. The metal-substrate bond is not well understood; the observed difference in adhesion between sputter deposited and photodeposited films indicates that the bond may be covalent. Finally, small quantities of metal carbonyls or other volatile organometallic precursors are available for many metals, and may be used to prepare electrodes of moderate size for testing, while precious metal sputtering targets are rather expensive and are inefficiently utilized. A sketch of the set-up for photodeposition is shown in Figure 1.

Alloys of rhodium-tungsten in compositions varying from  $\text{Rh}_3\text{W}$  to  $\text{RhW}_8$  have been made using  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $\text{W}(\text{CO})_6$  as precursor materials; different compositions were attained by adjusting the partial pressures of the rhodium and tungsten carbonyls in the deposition chamber during illumination. The electrical properties of these photodeposited films, determined as sheet resistance at room temperature, are similar to those of sputter deposited films. Sputter deposited  $\text{Rh}_3\text{W}$  typically has a room temperature sheet resistance of  $\sim 10 \Omega/\square$  (1). The  $\text{Rh}_3\text{W}$  electrodes made by PCVD had a room temperature sheet resistance of  $\sim 15 \Omega/\square$ .

In addition to developing a technique for photodeposition of alloys, we have used PCVD to make integral grids + electrodes. This approach takes advantage of the characteristics of photolytic chemical vapor deposition. Several previous studies of photodeposition have shown that, within certain intensity ranges, the metal deposition rate is directly proportional to the power of incident light (11). It has also been shown that metals will photodeposit preferentially at "pre-nucleation" sites, illumination which is not directed only at those sites (6). New nucleation sites may be formed by increasing the illumination intensity, thus depositing metal in the entire illuminated area. Integral grids + electrodes may be made by taking advantage of these characteristics of PCVD.

#### EXPERIMENTAL

Four electrodes  $1.2 \text{ cm} \times 0.8 \text{ cm}$  were deposited on a section of  $\text{Na}\beta''$ -alumina ceramic tube (Ceramtec) 8 cm long and 0.15 mm diameter. Two electrodes were  $0.5\text{--}1 \mu\text{m}$  thick and were made with grid lines  $6.8 \mu\text{m}$  thick by illuminating the ceramic through a mask in the presence of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $\text{W}(\text{CO})_6$  vapor. The output of a Quesetek 2340 excimer laser operating on at 248 nm ( $\text{KrF}$ ) was imaged through a positive mask. The mask was made on a UV grade fused silica optically flat window and was 95% transparent in regions where thick grid lines ( $\sim 6 \mu\text{m}$ ) were desired and was 10% transparent in regions where thin film electrode ( $0.5\text{--}1 \mu\text{m}$ ) was desired. Grid lines were  $220 \mu\text{m}$  wide and each thin film (electrode) area  $2.25 \text{ mm}^2$ . About 20% of the total electrode area was occluded by grid lines. With the known relationship of metal deposition rate to light intensity and the characteristic of pre-nucleation, electrode-grid combinations were possible.

Figure 2 shows the mask and Figure 3 shows an electrode with grid which was deposited on  $\beta''$ -alumina tube. The other two electrodes were made 0.5 - 1  $\mu$ m thick and were without grid lines. They were made by irradiating the  $\beta''$ -alumina tube through a wire mesh.

The organometallic precursors used are  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $\text{W}(\text{CO})_6$  (Aldrich). They were used as received. The vapor pressures of these compounds are not available, nor are they readily measured by usual techniques because the metal carbonyl poisons most gauges. The deposition rates of each material were determined for temperatures 25-70  $^\circ\text{C}$  and for laser energies of 150 - 250 mJ with repetition rates of 20-35 Hz.

It was found that the deposition rate for each material could easily be varied by adjusting the flow rate of the carrier gas while keeping the precursor materials at a fixed temperature of 40  $^\circ\text{C}$ . To obtain a Rh/W ratio of 3:1, carrier gas pressure in the chamber was adjusted to 150 mtorr for both tungsten and rhodium precursors. The chamber window was purged with a flow of buffer gas at 100 sccm the window, resulting in a total chamber pressure of  $\approx 1$  torr during deposition. Both carrier gas and buffer gas were 99.99% helium.

Deposition was accomplished by irradiating the substrate with a 1  $\text{cm}^2$  region of the output of the laser. The homogeneous portion of the beam was selected with a mask. The laser was operated at 150 mJ and 25 Hz. The energy incident on the substrate was 85 mJ/pulse. A thin layer of Rh metal was deposited by irradiating in  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  vapor only for 30 seconds before opening the chamber to  $\text{W}(\text{CO})_6$  vapor. This thin layer facilitated rhodium deposition. To make integral electrodes with grids, the substrate was irradiated for 45 minutes through a positive mask. To make electrodes alone, the substrate was irradiated for 10 minutes with no mask.

Electrodes were contacted by wrapping them in molybdenum screen (1/5 squares/cm) coated with platinum on the contact side. The screen was tied on the tube with 0.5 mm diameter molybdenum wire; a lead of the same wire was attached and insulated with  $\alpha$ -alumina.

Performance of electrodes without grids was compared with performance of electrodes with grids in a vapor exposure test chamber (VJ-ETC) with sodium vapor. The chamber has been described in detail previously (1, 12); briefly, it is a stainless steel chamber with a flange containing six feedthroughs for leads and thermocouples and a heater well which goes the length of the chamber, down the center. A section of BASF tube with several electrodes may be mounted on the heater well. 20 grams of sodium is added to the chamber after it is evacuated. The chamber is put in a tube furnace and heated; the sodium melts and stays in a pool in a well at one end of the chamber. The temperature of the sodium pool and thus the vapor pressure of sodium may be controlled by heating or cooling the well.

The electrodes on the BASF tube may be operated in pairs as a two electrode, non-power producing, electrochemical cell. Performance is measured by comparing voltammograms of the electrode-grid pair with voltammograms of the electrode without grid pair and by electrochemical impedance spectroscopy. Sodium transport

and electrode kinetics information as well as electrolyte resistance may be extracted from current-voltage data. A model which correlates performance in the exposure test chamber with a full AMTEC experiment has been developed (12).

## RESULTS AND DISCUSSION

It was found that laser energy and repetition rate must be kept relatively low in order to avoid ablation of the deposited metal. The laser pulse is 10 nsec; laser energies greater than 200 mJ and repetition rates greater than 30 Hz resulted in ablation of deposited material, as seen by evidence of melting in scanning electron microscopy and by apparently low deposition rates. Several authors have modeled the instantaneous temperature of substrates irradiated with pulsed lasers, and the predicted temperatures vary (13), but in any case the temperature will be  $> 3000$  K, high enough to melt both tungsten and rhodium.

An electron micrograph of the deposited  $Rh_3W$  film is shown in Figure 4. This micrograph shows the electrode to be  $\sim 0.5 \mu m$  thick, with grain diameters  $< 0.1 \mu m$ . According to the model for electrode lifetime based on extensive high temperature life tests developed at the Jet Propulsion Laboratory, this grain size is excellent for kmf-lived AMTEC performance (14). This  $Rh_3W$  electrode apparently has very low porosity; earlier studies have shown  $Rh_3W$  to have excellent sodium transport, as does this example, possibly along grain boundaries (15).

Room temperature measurements of the sheet resistance of the photodeposited electrodes made before operation did not show a significant difference between the electrodes with grids and the electrodes without grids. Both were  $10-15 \Omega/\square$ . Current-voltage curves in the VETC, shown in Figure 5, show a significant difference between the grid pair and the non-grid pair. These experiments are still ongoing, and so no further data on the differences between the electrodes are yet available.

## CONCLUSIONS

A technique for depositing metal alloy films on a solid surface has been developed and demonstrated. Photolytic chemical vapor deposition was used to make films with Rh/W ratios from 5 to .12; the ratio was changed by adjusting the flow rate of carrier gas for either the rhodium or tungsten precursor compound. Films  $0.5-1 \mu m$  thick with the composition  $Rh_3W$  were deposited on Na- $\beta$ -alumina solid electrolyte for testing as electrodes for use in the alkali metal thermal to electric converter. In addition to developing a technique for making alloy films, a technique for making current collection grids which are integral with the electrode has also been developed and demonstrated.  $0.5 \mu m$  thick electrodes which incorporate such grids, consisting of lines some  $220 \mu m$  wide and  $5-6 \mu m$  thick on  $2 mm$  centers, were made for a test to compare them with electrodes made by PCVD without grids. The testing process is still underway, and so final data on the comparison are not yet available.

## ACKNOWLEDGEMENTS

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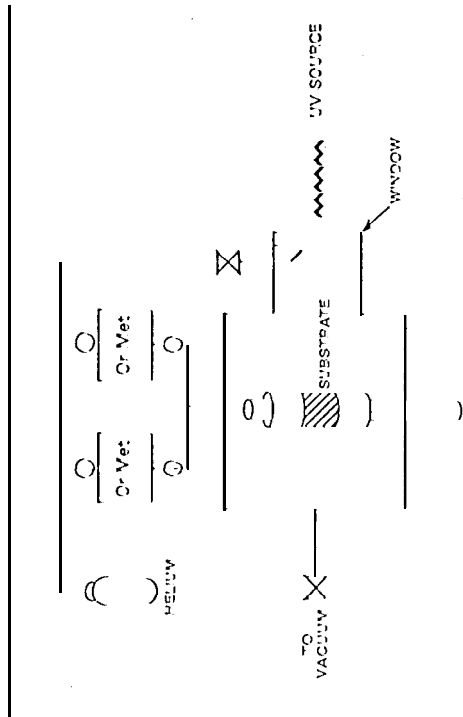


Figure 1: The setup for photochemical vapor deposition.

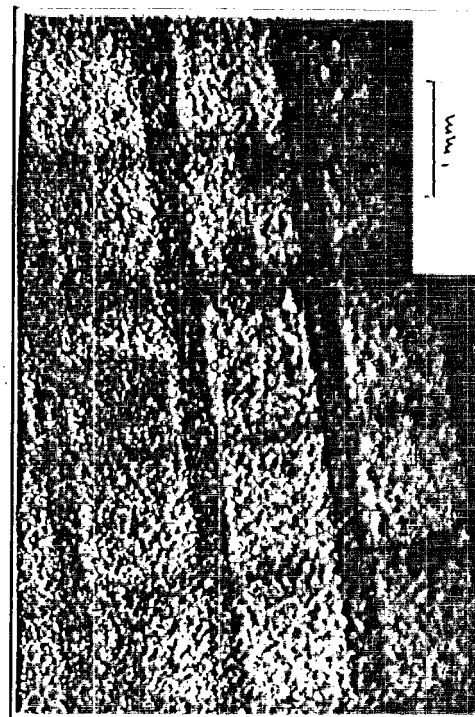


Figure 3: By irradiating through the positive mask (Figure 2a), an electrode with integral grids was made.

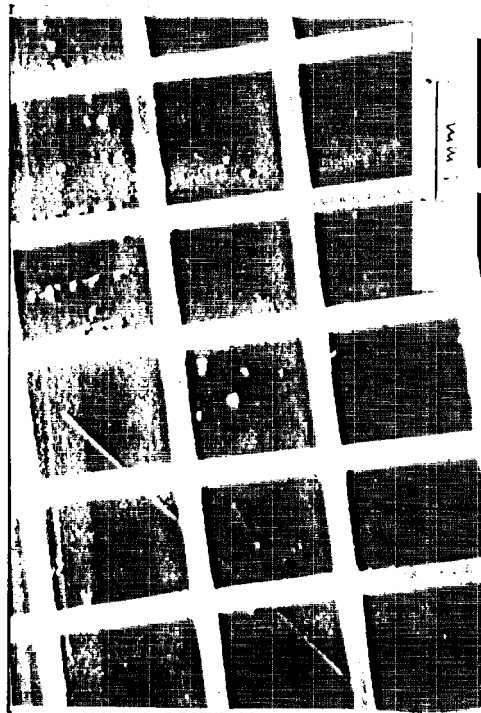


Figure 2a: A positive mask was used to image the laser beam for pCVD of  $\text{Rh}_3\text{W}$  electrodes with integral grids.

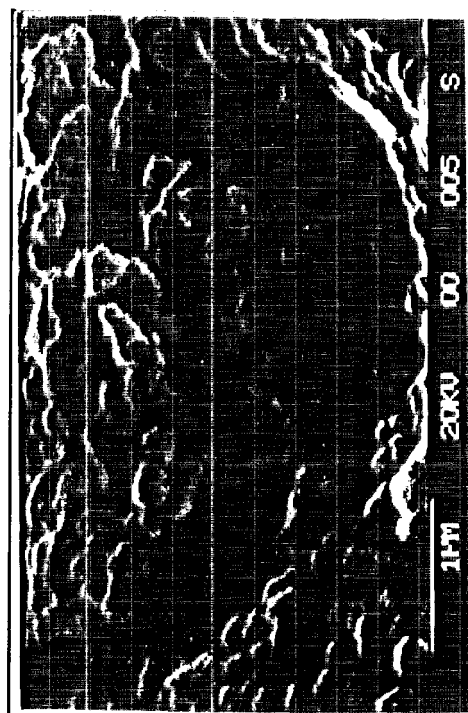


Figure 4: The grain size of thin films of  $\text{Rh}_3\text{W}$  deposited by pCVD is  $< 100 \text{ nm}$ ; grains are dense and electronic conductivity is good.

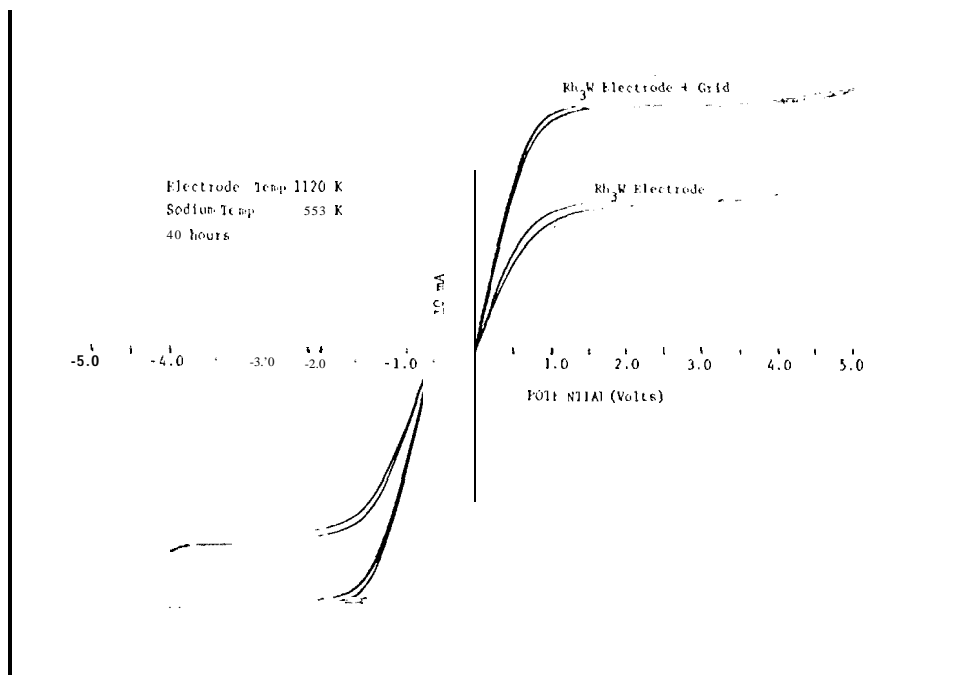


Figure 5: Current-voltage sweeps of Rh<sub>3</sub>W electrode pairs show a significant difference in performance between electrodes with grids and electrodes without grids.